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Journal of Polymer Science, Part B

Polymer Letters

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• C. G. Overberger • G. Smets

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PROF. KARL ZIEGLER —— PROF. GIULIO NATTA received the 1963 Nobel Prize in Chemistry for achieving control over the growth step in addition polymerization, thereby making possible the synthesis of stereoregular macromolecules.

The Editors and Publishers of the Journal of Polymer Science consider this honor a well-deserved recognition of two great scientists and also of the fact that polymer chemistry has now taken its place, along with analytical, inorganic, organic, and physical, as one of the important branches of chemistry. They extend their heartiest congratulations to Professor Ziegler and to Professor Natta.

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POLYMER LETTERS VOL. 1, PP. 649-654 (1963)

THE FREQUENCY DEPENDENCE OF THE GLASS TRANSITION

We wish to report some empirical correlations between the temperature of the dynamic mechanical loss maximum (dynamic glass transition temperature), T_d and the frequency of measurement, ν_d. Arrhenius plots (log ν_d versus $1/T_d$) were constructed, using data from the literature, for a number of polymers. First the data were found to be well represented by straight lines extending over a wide frequency range; however, more important, all the lines converged in either of two regions; corresponding to a ν_d of 10^8 cps. and a T_d of 454°K. (181°C.) for the more sterically restricted polymers and a ν_d of 10^{18} and a T_d of 562°K. (289°C.) for sterically nonrestricted polymers. Representing this, Arr-

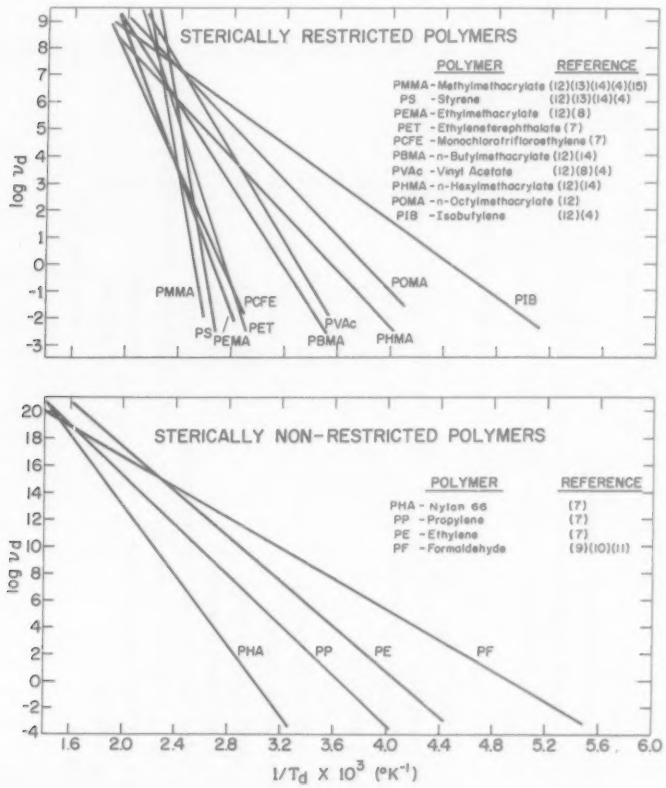

Fig. 1. Arrhenius plots for various polymers.

TABLE I

Test of Empirical Scheme Using Available Data

Polymer	T_d(cps.), °K.	Lit. ref.	ΔH_a, Kcal./mole	T_g(calcd.), °K.	T_g(lit.), °K.	Diff., °K.
		Sterically restricted polymers				
Isobutyl vinyl ether	272(1.2)	(4)	24 [e]	254	251 [c]	3
Methyl acrylate	298(1.2)	(4)	32	281	276	5
Ethyl acrylate	268(1.6)	(4)	23	249	251	−2
n-Butyl acrylate	241(0.8)	(4)	18	226	217	9
Vinyl chloride	363(0.7)	(4)	68	347	347	0
Hevea rubber (unvulc.)	223(1.2)	(4)	16	208	200	8
Polyurethane rubber	248(1.0)	(8)	20	234	237	−3
Bisphenol A carbonate	433(1.0)	(1)	333	423	433	−10
(ER): Diethylenetriamine [a]	418(100)	(5)	144	394	395	−1
(ER): Methylenebisorthochloroanaline	433(100)	(5)	250	414	422	−8
(ER): C_{36} aliphatic diamine	328(1.0)	(5)	43	311	320	−9
(ER): m-Phenylene diamine	440(1000)	(6)	326	423	463	−40
Acetaldehyde	254(0.58)	(15)	22	243	243	0
PMMA	(see Fig. 1) [b]		121	382	385	−3
PS	,,		129	373	373	0
PEMA	,,		57	342	338	4
PET	,,		67	348	342	6

PCFE	"		55	347	346	1
PBMA	"		33	296	300	−4
PVAC	"		37	289	303	−14
PHMA	"		27	264	268	−4
POMA	"		24	249	253	−4
PIB	"		16	210	202	8
	Sterically nonrestricted polymers [d]					
Hexamethylene sebacamide	333(4.0)	(16)	60	326	323	3
Ethylene oxide	218(0.40)	(15)	30	209	206	3
PE	(see Fig. 1) [b]		44	249	253	−4
PP	"		42	272	260	12
PF	"		26	189	190	−1
PHA	"		59	344	343	1

[a] (ER) designates epoxy resin.

[b] Data on these polymers were used to establish eqs. (1) and (2); $T_d(-1.5)$ was determined from the "free fit" least squares equation.

[c] Values obtained from literature data compiled by O. Griffin Lewis of the American Cyanamid Company's Stamford Laboratories.

[d] Sterically nonrestricted polymers are considered here as polymers containing no bulky atoms or sidegroups attached along a linear chain. Although polypropylene was included in this class (Fig. 1), its fit to the empirical scheme was poorest of those (of this class) tried.

[e] From eq. 1.

henius plots for some of these polymers are given in Figure 1. The existence of joint intersections among the two polymer types is broadly indicated. From this finding, empirical equations were derived relating the frequency dependence of T_d to the activation energy for the glass transition process, ΔH_a (cal./mole),

$$\log \nu_d/\nu_c = (-\Delta H_a/4.57)\,[1/T_d - C] \tag{1}$$

where for more sterically restricted polymers $\nu_c = 10^8$ and $C = 2.2 \times 10^{-3}$ and for the nonrestricted polymers $\nu_c = 10^{18}$ and $C = 1.78 \times 10^{-3}$. From further probing into these transition frequency-reciprocal temperature relationships, other empirical equations were discovered. When the T_d value corresponding to a hypothetical $\log \nu_d$ of -1.5 was plotted against the (dilatometric) glass temperature, T_g, a straight line resulted;

$$T_{d(-1.5)} = a\,T_g + b \tag{2}$$

which by least squares analysis gave, for the more sterically restricted polymers, $a = 1.074$ and $b = -22$ and for the nonrestricted polymers $a = 0.87$ and $b = 34$. By combining eqs. (1) and (2), an empirical equation results relating the activation energy ΔH_a and the "classical" glass transition temperature, T_g, which when reduced to its simplest form is:

$$\Delta H_a = (46.4\,T_g - 955)/(1.048 - 2.35 \times 10^{-3})\,T_g \text{ (restricted)}$$
$$\Delta H_a = (77.6\,T_g + 3030)/(0.94 - 1.55 \times 10^{-3}\,T_g) \text{ (nonrestricted)} \tag{3}$$

The discovery of eqs. (1) and (2) enables one to test the overall applicability of this approach using literature data where only one value of T_d (at a given ν_d) is reported. Using eq. (1) to calculate ΔH_a, the value for T_g can subsequently be estimated from eq. (3). This calculated value of T_g should equal the reported glass temperature (dilatometric, differential thermal analysis, etc.) for the polymer. Such a scheme was adapted to several polymers where values of T_d and T_g were available. In general, as indicated by Table I, the results of this analysis were surprisingly good considering that the experimental error involved in measuring either T_d or T_g is usually ± 5°C. In addition, the values of T_d and T_g were, in most cases, taken from different workers, furthermore, there was no discrimination as to whether the mechanical loss factor analyzed was reported as a log decrement, $\tan \delta$, $\pi G''/G'$, Q^{-1}, or an ultrasonic attenuation.

A generally accepted rule states that dynamic glass transition temperatures are about 10 to 15°C. higher than T_g. In comparison, it is found that the empirical scheme presented in this communication is somewhat better in predicting T_g from T_d than is the simple relation

$T_g = T_d - 13$. This simple rule holds best for T_d data in the range of 1 cps. and with polymers of an intermediate glass temperature (T_g = 230 to 400°K.). On the other hand, the empirical scheme using eqs. (1) and (3) is of general applicability with deviations independent of frequency. However, in a few instances, deviations between the calculated T_g and the observed values were greater than twenty degrees. For example, the correlation was poor for polymers with high glass transition temperatures. This observation suggests that limitations exist regarding the applicability of eqs. (1) and (2).

The theoretical implication of the common intersect behavior is that glass transition "critical points" may exist for certain types of polymers. For example, it is predicted here that no sterically restricted polymer should exhibit a glass transition above 454°K. (181°C.). Under these circumstances, ΔH_a would become infinite and the glass transition process could not occur. However, a few sterically restricted polymers have been synthesized which have glass transition temperatures above this "critical temperature." Among these are certain polycarbonates (1), poly(4,4-dimethyl-l-pentene) (2), and polybenzimidazole (3). Since these polymers all have stiff backbones the usual concept that the glass transition process involves the rotation of molecular segments becomes obscure. Therefore, in these cases one may expect a different mechanism for the glass transition process. Additional experimental work is needed to completely understand the nature of the glass transition condition of these high temperature polymers.

The author wishes to thank Dr. O. Griffin Lewis for his helpful suggestions during the course of this work.

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POLYMER LETTERS VOL. 1, PP. 655-657 (1963)

DENSITY AND DEGREE OF CRYSTALLINITY IN POLYMERS

Perhaps the most convenient way of estimating the degree of crystallinity in a semicrystalline polymer is afforded by the density method. In this, the overall density of a polymer sample is determined experimentally and then by making assumptions as to the nature of the crystalline and amorphous regions within the polymer, it is possible to calculate the magnitude of the crystalline fraction of the particular sample. The method offers considerable advantages of simplicity and rapidity, without the attendant complication of background correction associated with some other methods. On the other hand its usefulness may be restricted to the validity of the original assumptions.

Because of the advantages there has been widespread application of the technique in polymer science, and yet despite this, the literature does not always indicate the significance of a particular set of results. For example, at least three expressions have been quoted and used and, examination shows that they are not entirely equivalent (1-3). In practice, the differences which do arise are small and in fact may be less than experimental uncertainty, but nevertheless as will be shown, the differences are real if obtained from one set of experimental results and will have an influence at least at the second-decimal place level when comparison is to be made with corresponding results obtained by the use of alternative techniques.

The problem may be resolved by consideration of the derivation of possible equations. In the first place we may assume that a semicrystalline polymer is a two phase system and that each phase may be characterized by a unique density. (It is well recognized that for the amorphous phase the density may be an average value and not representative of any one submicroscopic region taken at random). We can then write

$$m = m_c + m_a$$

where m is the mass of a polymer sample and m_c and m_a are the masses of the crystalline and amorphous elements respectively. Substituting for density we obtain

$$d \cdot v = d_c \cdot v_c + d_a \cdot v_a$$

where the d and v terms refer to the densities and volumes of the relevant regions. Defining the volume fraction of the crystalline region as $x_v = v_c/v$ and substituting

$$d \cdot v = d_c \cdot v \cdot x_v + d_a \cdot v \cdot (1 - x_v)$$

and eliminating v and rearranging we obtain finally

$$x_v = (d - d_a)/(d_c - d_a) \tag{1}$$

This is of the form quoted by Frith and Tuckett (1) with the identification of crystallinity as that of a volume fraction.

Alternatively, if we write

$$v = v_c + v_a$$

and make substitution and rearrangement as before we obtain an analogous equation of the form

$$x_m = (V - V_a)/(V_c - V_a) \tag{2}$$

where x_m is the weight fraction of crystallinity and the V terms refer to specific volumes. This equation is identical to that used by Hunter and Oakes (2). Other relationships require a conversion of weight and volume terms (3).

It is a simple matter to show that the two equations are related as follows

$$x_m = (x_v \cdot d_c)/d \tag{3}$$

Thus it will be seen that from the same experimental results it is possible to derive two sets of estimations of the degree of crystallinity, both in themselves correct but exhibiting a difference in magnitude and implication.

This difference is given by $x_m - x_v$ and it is interesting to see the conditions for it to have a maximum value. Substitution in eq. (3) gives

$$x_m - x_v = x_v\,[(d_c/d) - 1]$$

Further substitution for x_v with subsequent expansion leads to

$$x_m - x_v = \frac{d_c + d_a}{d_c - d_a} - \left(\frac{d}{d_c - d_a} + \frac{d_a \cdot d_c}{(d_c - d_a) \cdot d}\right)$$

It follows therefore that this will have a maximum value for

$$\frac{d}{d_c - d_a} + \frac{d_a \cdot d_c}{(d_c - d_a) \cdot d} = \text{a minimum}$$

Differentiation with respect to d shows that $x_m - x_v$ will have its maximum when

$$d = (d_a \cdot d_c)^{1/2} \quad (4)$$

and that at this value of d the magnitude of this difference will be

$$x_m - x_v = \frac{(\sqrt{d_c} - \sqrt{d_a})^2}{d_c - d_a} \quad (5)$$

Applying this treatment to the case of polyethylene, for example, and using published values for d_c and d_a (2,4) it appears that the maximum discrepancy occurs at $x_v = 0.50$ and has a value of the order 0.04–0.05.

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POLYMER LETTERS VOL. 1, PP. 659-662 (1963)

THERMOCHEMISTRY OF INTERCHANGE REACTIONS IN CONDENSATION COPOLYMERIZATION

Introduction

Condensation copolymerization proceeds in the same way as in the formation of the simple homopolymers but the chains now consist of mixed units. It is often assumed that in the first place the reagents condense less randomly according to the relative reactivities of the endgroups and that the resulting low or medium molecular weight products rearrange as the reaction proceeds, finally giving a randomly arranged copolymer (1).

However, a quantitative theory of interchange reactions in condensation copolymerization has not been put forward. In this publication we present a new, simple, theoretical analysis which can reveal the interchange reactions in condensation copolymerization.

Theory

Consider the copolymers made up of two types of monomer units A and B. Copolymers have structures something like –A–CONH–B–CONH–A–CONH–B–CONH–B–CONH–A–CONH–B–CONH–A–CONH–A–CONH–A–CONH–B–. To treat the problem quantitatively, we shall now introduce a new parameter γ:

$$\gamma = [P_{AB} - (P_{AB})_{rand}]/[(P_{AB})_{max} - (P_{AB})_{rand}] \quad (1)$$

In this equation P_{AB} represents the number of A–B pairs in the actual copolymer; $(P_{AB})_{rand}$ represents the number of A–B pairs which would exist in a copolymer of the same composition if the copolymer were random; and $(P_{AB})_{max}$ represents the maximum number of A–B pairs which could exist if complete order occurred.

$(P_{AB})_{rand}$ is given by

$$(P_{AB})_{rand} = 2X_A X_B N_O \quad (2)$$

where X_A is the mole fraction of A in the copolymer, X_B is the mole fraction of B in the copolymer, and N_O is the total number of bonds. In the case of the altemating copolymer, where $X_A = X_B = 1/2$,

$$(P_{AB})_{max} = N_O \quad (3)$$

From eq. (2) for this copolymer

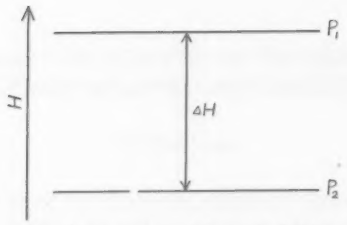

Fig. 1. Two-level systems with probabilities P_1, P_2.

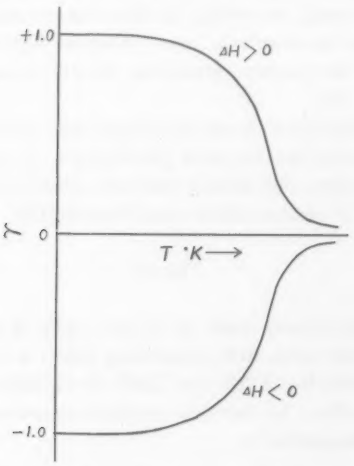

Fig. 2. γ-Parameter vs. temperature.

$$(P_{AB})_{rand} = N_O/2 \tag{4}$$

and hence from eqs. (1), (3), and (4) we obtain

$$\gamma = 2P_{AB}/N_O - 1 \tag{5}$$

Then the number of A–B pairs can be expressed as follows:

$$P_{AB} = N_O\,(1 + \gamma)/2 \tag{6}$$

Out of a total number of bonds N_O, the fraction of bonds of the A–B type is

$$f_{AB} = P_{AB}/N_O = (1 + \gamma)/2 \tag{7}$$

Consequently, the fraction of bonds which are like bonds is

$$f_{AA} + f_{BB} = 1 - f_{AB} = (1 - \gamma)/2 \tag{8}$$

The enthalpy of an A–B bond is H_{AB}, the enthalpy of a B–B bond is H_{BB}, the enthalpy of a B–A bond is H_{BA}, and the enthalpy of an A–A bond is H_{AA}. For a system with an equal number of A and B monomer units, $P_{AA} = P_{BB}$. If the average energy of like bonds $(H_{AA} + H_{BB})/2$ is greater than that of unlike bonds $(H_{AB} + H_{BA})/2$, we have then the simple energy level system indicated in Figure 1.

If the change in entropy for the reaction is zero, in thermal equilibrium, the relative probability of occupancy of the upper energy state P_1 to that of the low energy state P_2 is given simply by Boltzmann statistics

$$P_1/P_2 = \exp(-\Delta H/kT)$$

where k is Boltzmann's constant.

The probability of occupancy of the upper energy state is

$$P_1 = (P_{AA} + P_{BB})/N_O = f_{AA} + f_{BB}$$

Similarly the probability of the low energy state is

$$P_2 = P_{AB}/N_O = f_{AB}$$

From eqs. (7) and (8)

$$(1 - \gamma)/(1 + \gamma) = \exp(-\Delta H/kT) \tag{9}$$

where $\Delta H = (H_{AA} + H_{BB})/2 - (H_{AB} + H_{BA})/2$
and so

$$\gamma = \{1 - \exp(-\Delta H/kT)\}/\{1 + \exp(-\Delta H/kT)\} \tag{10}$$

In Figure 2, γ from eq. (10) is plotted versus temperature. If ΔH is positive γ will be positive and the monomer units will tend to alternate in the polymer. If ΔH is negative γ will be negative and the monomer units will tend to cluster in "blocks" in the copolymer. If ΔH is positive, at a temperature of 0°K., γ is predicted to be equal to 1, and at high temperatures to approach zero. If ΔH is negative, at a temperature of 0°K., γ is predicted to be equal to −1, and at high temperatures to approach zero. Therefore, in any case, it is observed that randomness becomes more predominant as the temperature is elevated.

In general, melt polymerization methods yield condensation copolymers with random distribution. In contrast, the method of interfacial polycondensation yields condensation copolymers ranging in order from

alternating to block arrangements (2), since no redistribution of groups will take place because of the low polymerization temperature as shown in Figure 2.

The author wishes to thank Dainippon Celluloid Company for permission to publish this work.

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TWO FORMS OF POLY(TETRAFLUOROETHYLENE) SPHERULITES AND THEIR SCATTERING PATTERNS*

In a previous publication from this laboratory (1), the anomalous low angle light scattering patterns obtained with poly(tetrafluoroethylene) (PTFE) films were described. It was pointed out that the patterns were consistent with an orientation of a principal axis of polarizability at an angle of 45° to the direction of maximum extension of the scattering entity rather than at 0° or 90° as with polyethylene and many other crystalline polymeric solids. The possibility of a relationship between this observation and the report (2,3) of a spherulite maltese cross (obtained using a polarizing microscope with crossed polaroids) oriented at 45° to the polarization directions was indicated. In this work, spherulitic PTFE films having both this 45° maltese cross as well as the normal 0° cross (oriented with the dark bands along the polarization direction) were prepared and their low-angle light scattering patterns were determined.

A few drops of TFE "Teflon" dispersion (obtained through the courtesy of Dr. Howard W. Starkweather, Jr., E. I. duPont de Nemours and Company) were spread on a microscope slide and allowed to air dry. The slide was then heated in an oven, cooled, and examined using a polarizing microscope or by light scattering using techniques which have been described previously (4,5) (with a cover slip and a silicone oil immersion fluid). The appearance of the film depended upon the time and temperature of heat treatment. The original dried dispersion contained isolated particles and gave circular V_v scattering pattern and no H_v pattern, as might be expected from the density fluctuations associated with scattering from dispersed spheres. With increasing time and temperature of heating, the particles coalesced and a ringlike V_v scattering pattern was obtained with still no H_v pattern. In times of the order of 1/2 hr. or more at 425°C., 45°-type spherulites were obtained upon rapidly cooling (Fig. 1). While at higher temperatures (425°-450°C.), 0° spherulites were obtained (Fig. 2). The 45° spherulites gave V_v and H_v scattering patterns of the sort previously reported (Fig. 3) while the 0° spherulites gave scattering patterns more like those for polyethylene (Fig. 4). Both the scattering patterns and the microscope appearance are consistent with orientation of the principal polarizability direction at 45°, to the spherulite radius in the 45° spherulite, and parallel or perpendicular to the radius in the 0° spherulites. Samples slowly cool-

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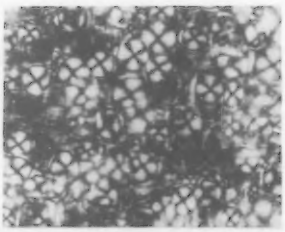

Fig. 1. A 45°-Type PTFE spherulite between horizontal and vertical crossed polarizers.

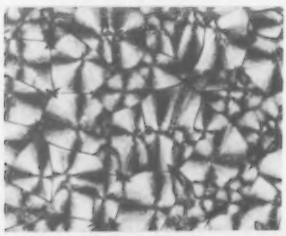

Fig. 2. A 0°-Type PTFE spherulite between horizontal and vertical crossed polarizers.

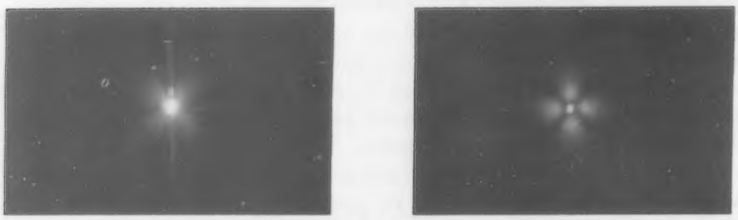

Fig. 3. V_v (left) and H_v (right) scattering patterns obtained from 45°-type PTFE spherulites.

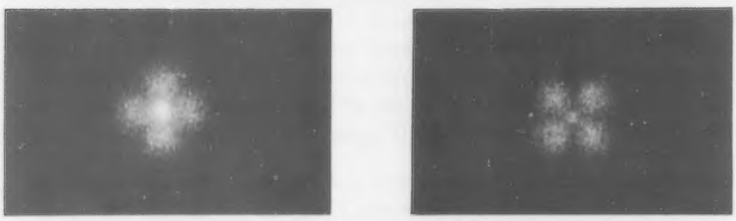

Fig. 4. V_v (left) and H_v (right) scattering patterns obtained from 0°-type PTFE spherulites.

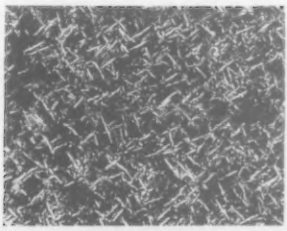

Fig. 5. Rodlike aggregates obtained from a film heated to 400°C. for 4.5 hr. and slowly cooled to room temperature.

Fig. 6. 45°-Type PTFE spherulites exhibiting ring structure.

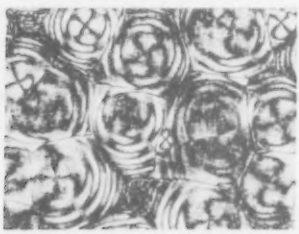

Fig. 7. "Swastika" type extinction cross in PTFE spherulites believed to be undergoing internal orientational transition.

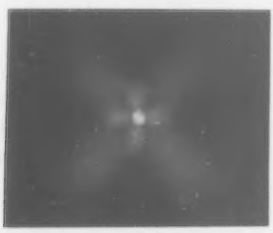

Fig. 8. An H_v scattering pattern from a preparation exhibiting "mixed" 0°- and 45°-type orientation.

ed from the oven temperature often showed rodlike aggregation (Fig. 5) rather than the spherulitic structure, but this still can give a spherulite-type scattering pattern as was the case in the previous report (1) and may result from anisotropic rodlike crystalline aggregates with the principal polarizability axis inclined at an angle to the rod axis. X-ray diffraction patterns indicated that the crystal structure was the same in both types of spherulites.

It is apparent that two varieties of 45° spherulites are possible; where the larger polarizability direction is either at +45° or –45° to the radius. Examination of the retardation colors using a first-order red plate indicated that this was indeed the case, where both types of spherulites are present in approximately equal numbers. In fact, some preparations exhibited ring structure (Fig. 6) where the rings represent alternations of orientation of this maximum polarizability direction between discrete values of +45° and –45° to the radius.

If the optic axis of the uniaxial PTFE crystals is permitted to lie out of the plane of the spherulite, then the alternation of orientation can arise from the helicoidal rotation of the 45° tilted optic axis about the spherulite radius (6) giving rise to extinction patterns of the type described in the literature (7-9). The spherulites having the 45° cross without rings are those where the growth temperature and time was high enough so that the spherulite radius exceeded the period of rotation, while those surrounded by rings continued to grow with decreasing rotational period as the growth temperature was lowered. Careful examination of the rings in preparations like that of Figure 6 reveals a zig-zagging of the rings as predicted by theory. This is particularly evident in Figure 7 which shows "swastika" type maltese crosses probably resulting in part from this rotation and in part from growth over a range in temperature where the angular orientation of the optic axis with respect to the radius may have varied during growth. Light scattering patterns of the type shown in Figure 8 which show a superposition of the two types of patterns probably result from samples undergoing transition in the orientation of crystals within spherulites.

While the results reported in this paper were obtained on samples made from sintering dispersions, similar results have been found with commercial "Teflon" films and on sections of molded samples indicating that the results were not surface artifacts but are typical of internal structure.

Scattering patterns similar to those found for the 45° spherulites are found for poly(trifluorochloroethylene) and fluorocarbon copolymer preparations having no microscopically resolvable spherulite structure. It is suggested that the crystal ordering within these polymers is similar to that occurring within the 45° spherulites.

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THE DETERMINATION OF NUMBER-AVERAGE MOLECULAR WEIGHTS OF POLYMERS USING FLUORESCENCE SPECTROSCOPY

An interesting paper, which appears to be a simple, precise, and rapid analysis, concerning the determination of M_N for polystyrene and polyisobutylene by means of fluorescence spectroscopy was published by Heintz (1). Our letter presents a more generalized expression which was derived from this paper. The fact that a singular relationship was obtained for two linear addition polymers having widely different chain attachments may imply that the method is applicable to a large variety of polymer types. Other equivalent expressions are derived which show the versatility of fluorescence spectroscopy.

Heintz's method involves measurement of the decrease in the intensity of fluorescence upon the addition of trace amounts of polymer to a rhodamine B dye-chloroform solution. Concurrently, the intensity of the absorption band for the dye at 5540 A. was proportionately reduced. This infers that the polymer is acting as a screen which is obstructing the amount of light energy that the dye can absorb. A plot of $[(F_0/F) - 1]$ versus polymer concentration is linear up to 0.002 g. of polymer/cc. The terms F_0 and F refer to the fluorescent intensity before and after the addition of the polymer, respectively. When the slope of this line was plotted against the square root of the number-average molecular weight for the particular polymer studied, the following relationships were obtained by Heintz:

Polystyrene:

$$[(F_0/F) - 1]/C = 0.163 \sqrt{M_N} \tag{1}$$

Polyisobutylene:

$$[(F_0/F) - 1]/C = 0.214 \sqrt{M_N} \tag{2}$$

The number-average molecular weight (as determined by osmometry) varied over the range 106 to 1.5×10^6 for these polymer samples.

It is possible to derive a more generalized expression (apparently valid for certain linear addition polymers) by introducing M_0, the statistical mass unit:

Polystyrene:

$$[(F_0/F) - 1]/C = 0.163 \sqrt{M_0} \sqrt{M_N/M_0} = 1.17 \sqrt{M_N/M_0} \tag{3}$$

Polyisobutylene:

$$[(F_0/F) - 1]/C = 0.214 \sqrt{M_0}\sqrt{M_N/M_0} = 1.13 \sqrt{M_N/M_0} \quad (4)$$

The value of M_0 depends on the structural unit used to define the number of segments (or bonds) per molecule. Since there are two C–C bonds per monomer along the polymer chain, M_0 is taken as one half the molecular weight of the monomer. The relationships expressed in eqs. (3) and (4) appear to be independent of sidechain substituents and can be expressed further or more generally as:

$$[(F_0/F) - 1]/C = 1.15 \pm 0.02 \sqrt{M_N/M_0} = 1.15\, \bar{h}/\beta = 1.15 \sqrt{\sigma} \quad (5)$$

where $\bar{h}$ = statistical average end-to-end distance of a polymer chain, β = segment distance or effective bond length, and σ = number of segments (or bonds) per molecule. If this proves to be applicable to other linear addition polymers, then the dependence of the fluorescence intensity on polymer concentration is strictly a function of the number of chain segments or the number of bonds per molecule.

Since the dimensions of the polymer chain as calculated from M_N/M_0, assuming a statistical average end-to-end distance, are a function of polymer solvation, the proportionality constant in eq. (5) may, therefore, vary with molecular size. From viscosity measurements, it has been shown (2) that the effective radius (R_e) of a solid sphere was related to the radius of gyration (R_G) of a polymer chain by the expression:

$$R_e = \gamma R_G \quad (6)$$

The values for γ range from 0.775 to 0.86 where a good solvent has the lower value. It would be interesting to note whether the use of good or poor solvents would change the proportionality constant of eq. (5) in the same proportion. Although no further experimental work has been reported, this method of determining M_N appears to be an accurate and versatile laboratory procedure.

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NUCLEAR MAGNETIC RESONANCE OF SOLID TRIOXANE

Recently, it has been found that trioxane polymerization can be induced by radiation in solid phase and that its polymer yield greatly depends on a temperature to which trioxane is subjected after irradiation (1-4). These facts suggest that molecular motion in a crystal of trioxane has an important role in polymerization.

To investigate the internal motion, measurements on proton magnetic resonance were carried out for polycrystalline trioxane with changing temperatures. Both the line width, defined by outer peak-to-peak sepa-

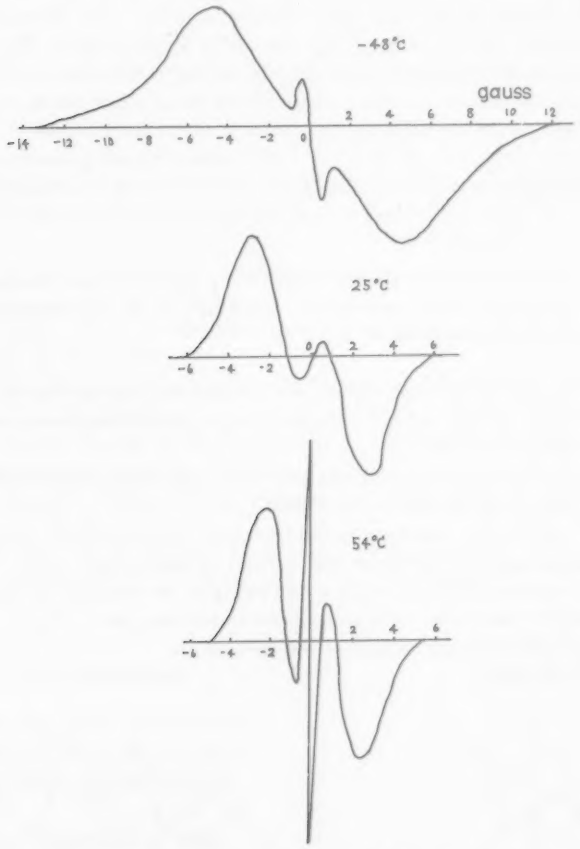

Fig. 1. Absorption derivatives of trioxane.

TABLE I

Observed Values of Second Moment and Line Width

	Temperature range, °C.		
	−70 ~ −10	20 ~ 40	45 ~ 62 (m.p.)
Second moment $<\Delta H^2>$ in gauss^2	12	3.9	3.0
Line width ΔHmsl in gauss	10	6.0	5.0

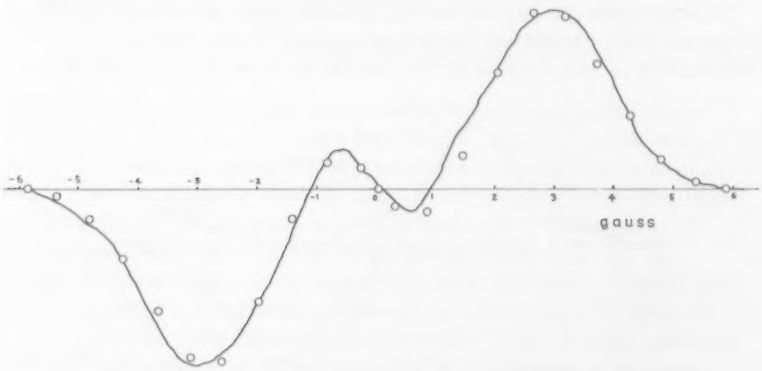

Fig. 2. Plot of theoretical calculation for polycrystalline trioxane undergoing chair-chair interconversion. Solid line is the experimentally recorded absorption derivative at 25°C.

ration of absorption derivative, and the second moment of absorption line have three steady values corresponding to three temperature ranges, which are listed in Table I.

Observed absorption derivatives have fine structures characteristic of these temperatures, as shown in Figure 1.

Below −10°C. the expected second moment agrees with the observed value, indicating that the molecular crystal is effectively rigid. The molecular motion likely to cause a narrowing of the absorption line is considered for two cases: rotation of the molecules about their C_3 axes and chair-chair interconversion of the molecules.

rotation interconversion

The arguments are essentially concerned with the two-spin system

with spin 1/2. Gutowsky and Pake have given the spectral line shape arising from spin pairs which rotate about a fixed axis (5). In our work the spectral line shape for the case of interconversion has been obtained by assuming that the proton pairs undergo a sinusoidal oscillation about the axis perpendicular to the pair direction. For this case, the theoretical shape of the absorption derivative coincides satisfactorily with the derivative observed at 25°C., as shown in Figure 2. However, for the case of rotation, theoretical and experimental curves do not fit together. The second moment is calculated for the case of interconversion, using the formula derived by Andrew (6), to be 3.8 gauss^2 in good agreement with the experimental value of 3.9 gauss^2.

In the highest temperature range, both the experimental line shape and second moment may be ascribed to the molecular motion as follows: the molecules engage in the chair-chair interconversion under rotational motion about their C_3 axes, and at the same time a part of them, taking a boat conformation, rotate about the axes perpendicular to the ring plane; in particular the latter motion gives a sharp central peak of absorption.

The highest temperature range concerned corresponds to temperatures in which the polymer yield of irradiated trioxane shows a great increase with increasing temperature (1-4).

A detailed discussion of this work will appear in a subsequent issue of the Journal of the Physical Society of Japan.

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MELTING TEMPERATURE DEPRESSION OF MELT-CRYSTALLIZED POLYETHYLENE WITH LAMELLA THICKNESS

Lately, we have been studying the properties of polymer specimens which are produced by the oriented-crystallization method from the melt. The method was first applied to polyethylene and specimens with sharp b-axis orientation were furnished for the purpose of x-ray small angle studying. The relation between the large spacings obtained from the equatorial low angle reflections and the linear growth rate was discussed (1), and in this work as well as in preceding studies, we attempted to measure the melting temperature of specimens with known lamella thickness. The results are briefly shown in this letter.

The method of oriented-crystallization is essentially based on the following principle, though the details will be reported in a succeeding paper. The crystallization is begun by pulling a specimen rod, which is enclosed in a glass capillary, with a constant speed along a steep temperature slope. The temperature slope extends from the room temperature up to temperatures sufficiently higher than the melting range. Owing to the steep slope, new nucleations can be prevented from occurring in the place near the growing front. Thus, the whole specimen rod comes to possess a single-spherulitic structure with the b-axis orientation as in the case of polyethylene. As most polymer spherulites have negative values of temperature dependence of the linear growth rate, the crystallization is proceeded stably and isothermally at a definite position in the temperature slope, that is, at a definite temperature T_c corresponding to the position, for a given pulling speed of the specimen rod u. Accordingly u is just equal to the linear growth rate of the spherulite. With the customary methods of crystallization it is generally difficult to prepare a specimen with an over-all uniform T_c in the low temperature range. By this method, however, it may safely be said that T_c is uniform even for larger u, that is, for lower T_c, as far as the b-axis orientation can be confirmed by the x-ray diffraction study. The crystallizing temperature can be changed by changing u, thus providing specimens with various crystallization temperatures, accordingly with various lamella thickness.

By the above method of crystallization, b-axis oriented specimen rods of linear polyethylene, Marlex 50, about 1 mm. in diameter, were produced for u values ranging from 0.07 to 40 mm./hr. After the large spacings were measured by the x-ray low-angle reflections, they were submitted to the melting temperature determination by the following method.

The specimen rod enclosed in a glass capillary was heated up to the melting temperature with a constant rate (1.2°C./min.) in a furnace of

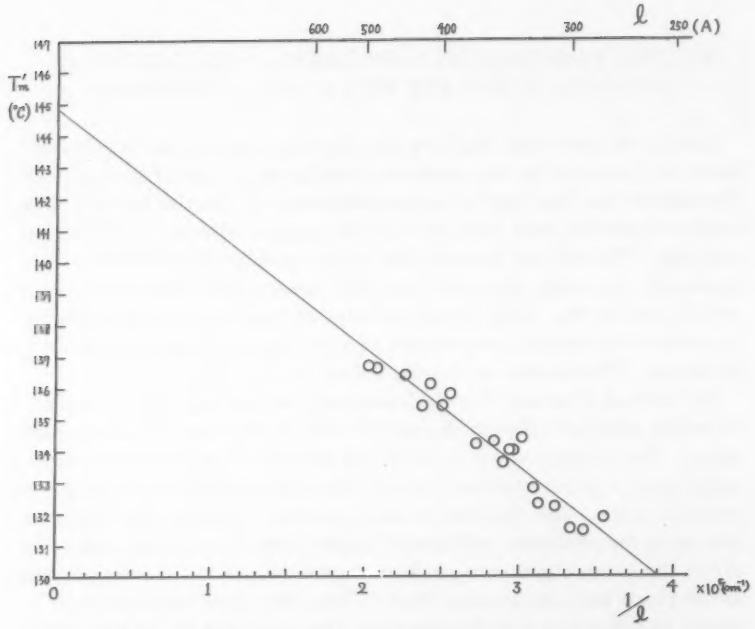

Fig. 1. Plot of melting temperature against inverse large spacing (Marlex 50).

small copper block, and the transmitted light beam from a tungsten lamp was detected with phototransistors. Transmission-temperature curves were recorded on a recorder chart and the saturation points of these curves corresponding to the attainment of liquid transparency were regarded as the melting point T_m.

Here, we should not disregard the effect of thickening of lamella by annealing during the period of heating, which might cause the rise of melting temperature. To avoid this effect we tried to adopt faster heating rates. In these cases, however, as the result of heat absorption accompanying the melting process, the momentary temperature difference between the specimen and the furnace were so large that the accurate T'_m was hardly possible to find. By measuring the temperature difference directly with a thin thermocouple, it was found in the case of our apparatus that the heating rate of about 1.2°C./min. is almost the maximum permissible rate for keeping the result in the limit of admittable errors. Consequently we were constrained to use this heating rate, and we employed the method of measurement to start with this heating rate from very near (about $1 \sim 2$°C. lower temperature) the estimated melting point, allowing the specimens little time to cause thickening until melting is reached.

The result is that, as is generally known for polymer substances, the larger the spacing, the higher the melting temperature. Plotting T_m' against the inverse large spacing 1/l, it may be possible to compare the result with the equation which has been derived for the melting point of a single crystal by Lauritzen and Hoffman (2) (Fig. 1). Here, we must assume that also the melt-crystallized specimen has the lamellar structure as do single crystals and that the large spacings from the low-angle reflections are considered to correspond to the thickness of the lamellae:

$$T_m' = T_m [1 - (2\sigma_e/l\Delta h)]$$

where T_m is the melting temperature of a lamella with infinite thickness, Δh is the heat of fusion per unit volume, σ_e is the surface free energy of the surface containing loops, and l is the thickness of the lamella. In accordance with this equation the straight line of Figure 1 can give, from the intercept the value of T_m, 144.8 ± 0.5°C. It also gives the value of σ_e from the slope, which is 127.1 ± 3.0 erg/cm.^{2}, by employing the value $\Delta h = 2.8 \times 10^9$ erg/cm.^{3} (2).

The obtained value of T_m is fairly near 143.1°C., which was found by Eby and Brown for linear polyethylene (3), and also the value of σ_e does not largely disagree with other recent estimates (2,4-6).

The authors wish to express their thanks to Professor Motowo Takayanagi of Kyushu University and also to Dr. Tsuneo Seto of Kyoto University for helpful advice and discussion.

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THE SWELLING OF PLEXIGLAS IN HYDROGEN PEROXIDE

The action of concentrated hydrogen peroxide on poly(methyl methacrylate) (Plexiglas) results in considerable swelling and softening, accompanied generally by appearance of a milky turbidity. A preliminary study of this phenomenon, twenty years ago (1), had led to a patent (2) covering the strainless shaping, at room temperature, of Plexiglas articles. Qualitatively the action of hydrogen peroxide is much more important and rapid than that of other liquids such as water and alcohols. In an attempt to understand the nature and the mechanism of this process we have investigated it by the spectroscopic and analytical methods.

The Infrared Spectra

The absorption of Plexiglas in infrared was measured first by Wells (3) and later, in greater detail, by Thompson and Torkington (4) who assigned most of the bands in the spectra to vibrations of specific groups of atoms. Very thin samples are required because of the strong absorbancy of this material. We used films about 25 μ thick in the 650 to 1500 cm.$^{-1}$ region, and films roughly four times as thick in the higher frequency range. Since the commercial product (Rohm & Hass Co.) is not available in such thin form, and since mechanical reduction would certainly be difficult, we resorted to the usual technique of evaporation of a solution in vacuo over a liquid mercury surface. Traces of the solvent, chloroform, may have remained in the polymer as shown by the following observations: (a) microscopic bubbles were visible in the films under strong (450 ×) magnification; (b) a weak infrared band was observed at 655 cm.$^{-1}$ (Fig. 1) which is missing in the previously reported spectra of poly(methyl methacrylate) (4). On treatment with hydrogen peroxide or methanol this band disappeared gradually; at the same time

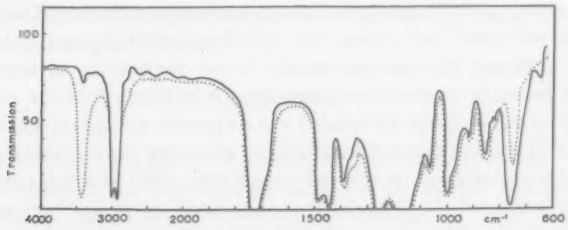

Fig. 1. Infrared absorption spectrum of a thin film of Plexiglas before (—) and immediately after (····) swelling in concentrated hydrogen peroxide.

TABLE I

Frequencies of the O–H Stretching Bands in Various Media

	H_2O_2		H_2O	
	Freq., cm.$^{-1}$	Ref.	Freq., cm.$^{-1}$	Ref.
Vapor	3610	(6)	3756 3652	(7)
Solution in CCl_4	3554	(6)	3710	(6)
Inert matrix	3578 3417	(8)	3725 3627	(9)
In Plexiglas	3410		3650 3550	
Liquid	3360	(6)	3390	(10)
Solid	3290 3180	(11)	3250	(10)

the 760 cm.$^{-1}$ band of Plexiglas decreased in intensity down to a certain minimum. Both phenomena were irreversible. Now chloroform has two strong bands at precisely 760 and 665 cm.$^{-1}$ (5); its other strong bands fall in regions of complete absorption of Plexiglas.

The films were immersed in liquid hydrogen peroxide (Becco's 95 to 99%) at room temperature for 3 hr., i.e., more than enough to reach saturation. After removal, they were dried quickly with filter paper and mounted between two discs of optical silver chloride. The most conspicuous change in the infrared spectra (Fig. 1) is a strong, fairly sharp peak at 3410 cm.$^{-1}$ due to the hydrogen peroxide absorbed in the polymer; the other main bands of hydrogen peroxide at about 2800 and 1350 cm.$^{-1}$ (6) were barely noticeable as shoulders on neighboring Plexiglas bands. It is interesting to compare the present O–H stretching frequency with those of hydrogen peroxide in various conditions (Table I). From the observed shifts it is clear that the absorbed H_2O_2 molecules are not "free," although the hydrogen bonds do not seem quite as strong as in the pure peroxide in condensed phases. It is likely that the carboxyl oxygens of the polymer molecules act as proton acceptors in this case. Films of Plexiglas treated with boiling water for long periods (8 hr.) eventually showed two very weak peaks near 3550 and 3650 cm.$^{-1}$; with absolute methanol the O–H band appeared at 3550 cm.$^{-1}$ (comp. 3340 cm.$^{-1}$ in the liquid (12) and 3682 cm.$^{-1}$ in the vapor).

When the treated films were left exposed to the air all the infrared bands due to the absorbed liquid disappeared gradually, a confirmation that the phenomenon is entirely reversible and causes no chemical alter-

ation of the polymer. Intensity measurements on the O–H bands as a function of time were used to evaluate the rate of diffusion of the various liquids used, as explained below.

Analytical Study

The extent of swelling of Plexiglas was determined by macroscopic measurements. In a typical experiment samples of the commercial plastic about 40 × 15 × 3 mm. were soaked in 98% H_2O_2 until complete saturation at room temperature, which required 6-7 days. This increased their weight by nearly 50% and their volume by about one third. Desorption was followed by placing the swollen samples in distilled water (10 ml.) which was titrated for H_2O_2 after periods of 24 hr. and replaced by a fresh supply of distilled water. Under these conditions the diffusion of the peroxide followed Fick's law, with a coefficient $D = 3.5 \times 10^{-4}$ cm.^{2}/min. This is much larger than the coefficient for diffusion in air, estimated from the rate of disappearance of the O–H band in the thin films, namely 9×10^{-8} cm.^{2}/min.

Since the diffusion coefficient of hydrogen peroxide has not been measured by the usual sorption-desorption method the above value of the coefficient cannot be compared directly. However, we estimated the diffusion of water in the same conditions from the rate of disappearance of the band at 1650 cm.$^{-1}$. The result, 3×10^{-8} cm.^{2}/min., agrees fairly well with those reported recently in the literature, namely 2.5 (13) and 1.6×10^{-8} cm.^{2}/min. (14). It is remarkable that hydrogen peroxide diffuses more rapidly than water in Plexiglas, although its molar volume is nearly double. The explanation must rest on the fact that there is a slight decomposition of the peroxide which expands the polymer lattice and weakens the crosslinking between the chains. Evidence for this may be seen in the appearance of a milky turbidity in the peroxide treated Plexiglas, which under strong magnification is seen to be due to myriads of tiny bubbles of even size. Also, the total peroxide desorbed in water is slightly less (3 to 4%) than that of the absorbed peroxide.

Although no measurements were made on this effect, the rate of swelling of Plexiglas in hydrogen peroxide was found to be faster the greater the concentration of the latter.

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TRIPHENYLSILYLLITHIUM AS A POLYMERIZATION INITIATOR

Triphenylsilyllithium (1,2) is a unique organometallic-type compound containing a silicon-lithium bond, rather than carbon-lithium. Triphenylsilyllithium has been reported to add to certain olefinic linkages, such as 1,1-diphenylethylene (3), triphenylethylene (3), and trans-stilbene (4), to form the corresponding triphenylsilyl-substituted compounds.

Triphenylsilyllithium, prepared by the cleavage of hexaphenyldisilane by lithium metal in tetrahydrofuran (5), was found to be highly reactive as a polymerization initiator. The results with several monomers are shown in Table I.

Infrared absorption spectra of typical polymers from each monomer were scanned. When not obscured by other bands, a very weak absorption was noted at 9.05 μ. This is probably the silicon-phenyl grouping, weak absorption due to low concentration of silicon in the polymer. An emission spectrograph of ashed polyisoprene (0.31% ash) indicated the ash contained greater than 10% silicon. Gravimetric silicon analysis of polyisoprene gave lower values than anticipated; however, silicon was a part of the polymer since the analyses did not change after several reprecipitations from isopropyl alcohol.

The molecular weight of a sample of polyisoprene (inherent viscosity 0.32) was found to be 16,500 by ebulliometric measurement. An approximation of 16,600 can be made from inherent viscosity data.* The close agreement is indicative of a narrow molecular weight distribution and suggests rapid initiation. Transfer steps should not be significant.

The microstructure of polymers initiated by the tetrahydrofuran solution of triphenylsilyllithium is similar to polymers prepared by organolithium initiation in the presence of small amounts of ethereal solvents.† Although definite proof of silylanions is lacking, the aforementioned results suggest that polymerization is initiated by rapid anionic attack on monomer.

Experimental

General Polymerization Procedure. Polymerizations were conducted in 7-oz. beverage bottles with 10 g. charges of monomer. Warm, oven-

*$\eta = 5.02 \times 10^{-4} M^{0.677}$ from Flory (6). Although intrinsic viscosity is employed for molecular weight estimations, inherent viscosity data are sufficient for approximations.

†For example, Kuntz and Gerber (7) reported 51% 1, 2-addition, 24% trans-1, 4 and 25% cis-1,4 for polybutadiene initiated by isobutyllithium in the presence of 0.5 vol.-% of tetrahydrofuran.

TABLE I

Triphenylsilyllithium Initiated Polymers

Monomer	Solvent	Vol.-% THF [a]	Initiator, mmoles [b]	Temp., °C.	Induction period, min.	Yield, %	Microstructure, %				Inherent viscosity
							cis	trans	1,2-	3,4-	
Butadiene	Toluene	0.80	4	50	0–10	100	19.7	21.7	58.6	–	1.06
Isoprene [c]	Pentane	0.75	5	50	0–60	100	20±5	15±5	–	55.0	0.51
Styrene	Toluene	0.20	1	50	0–10	100	–	–	–	–	0.60
Methyl methacrylate	Toluene	1.0	5	–25	0	43.0	–	–	–	–	0.80
Acrylonitrile	Toluene	2.0	10	–65	0	34.7	–	–	–	–	0.62

[a] Volume of THF added as the initiator solution.

[b] Millimoles of initiator as a tetrahydrofuran solution/100 g. monomer.

[c] A polymer prepared at 30 mmoles initiator/100 g. monomer was divided into 3 parts. The control was designated as A. B was reprecipitated twice from isopropyl alcohol; C was reprecipitated 4 times. The gravimetric analysis for wt.-% of SiO_2 reported was: A, 0.05; B, 0.03; C, 0.05.

dried bottles were cooled in a nitrogen stream prior to charging with either n-pentane or toluene solvent. The n-pentane was then purged for one minute with nitrogen gas at three l.p.m.; the toluene solvent for five minutes. Monomer, followed by initiator, was charged by means of a syringe through self-sealing rubber gaskets fastened by crown caps. The bottles were pressured to 25 p.s.i. with nitrogen gas. Subsequent to completion of reaction, the polymers were coagulated in isopropyl alcohol and protected with 1% antioxidant.

The polymer microstructure for polybutadiene (8) and polyisoprene (9) were determined by infrared techniques.

The infrared spectrum of a representative polymer sample for each monomer was scanned either as a carbon disulfide solution or as a KBr pellet. Weak absorption was observed in the 9.0-9.1 μ area. This area was obscured for polymethyl methacrylate. Polyacrylonitrile also possessed a prominent absorption peak at 4.45 μ, indicative of the nitrile grouping.

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HYDROLYSIS OF POLY(VINYL ACETATE)S OF VARIOUS TACTICITIES

The relation between chemical reactivity and steric structure of high polymers has recently received considerable attention with the development of stereochemistry of high polymers. The rate of hydrolysis of poly(vinyl acetal) was shown to be markedly affected by the tacticity of the original poly(vinyl alcohol) (1). For poly(vinyl alcohol) and its derivatives, no data showing different chemical reactivities affected by the tacticity of the polymers had been obtained. However, in various acrylic polymers abundant data showing the different hydrolytic reactivities affected by their tacticities have been reported (2-5). At this time, hydrolysis of poly(vinyl acetate) (PVAc) samples of various tacticities have been studied. Because of the autocatalytic nature of the reaction (6,7), it may be expected that the tactic structure of the polymer could influence the reaction.

All PVAc samples used in the experiment were prepared by acetylation of poly(vinyl alcohol) with acetic anhydride in pyridine. Acetylation was repeated twice. Infrared and elemental analyses and ester value showed that the acetylation was essentially complete. Preparative conditions and structural parameters of the original poly(vinyl alcohol) samples are summarized in Table I.

Alkali-catalyzed hydrolysis was carried out in a homogeneous system (70% dioxane/water) at 30°C. Concentration of the polymer was 0.018 base mole/liter and that of sodium hydroxide was 0.02N. The rate of hydrolysis was determined by following the alkali consumption. Time-conversion curves are shown in Figure 1. These curves were analyzed by applying the following empirical formula (10) and, consequently, the initial rate constant, k_0, and degree of acceleration during the reaction, m, were determined. (See Table II).

$$dx/dt = k(a - x)(b - x), \text{ and } k = k_0(1 + mx/a)$$

where a = initial concentration of acetyl group, b = initial concentration of sodium hydroxide, x = concentration of acetyl group reacted in time, t.

A check on the adaptability of the equation was made by a comparison of experimental data with time-conversion curves calculated from the following integral equation with the derived k_0 and m as shown in Figure 2.

$$\int [dx/(1 + mx/a)(a - x)(b - x)] = k_0 \int dt$$

Initial rate of stereoblock PVAc derived from stereoblock poly(vinyl

TABLE I

Preparative Conditions and Structural Parameters of Original Poly(vinyl Alcohol) Samples

No.	Polymerization				Conversion to poly(vinyl alcohol)	Poly(vinyl alcohol)	
	Monomer	Medium	Temp., °C.	Initiator		DP	D_{916}/D_{850} [b]
1	Vinyl tert-butyl ether	Toluene	− 78	$BF_3(C_2H_5)_2O$	Acetylation with acetic anhydride and $BF_3(C_2H_5)_2O$ followed by alkaline hydrolysis	1000	0.02
2 [a]	Vinyl formate	None	− 78	γ-Ray		370	0.28
3	Vinyl acetate	None	120	ABIN	Alkaline hydrolysis	1600	0.36
4	Vinyl formate	Methyl	− 78	$B(C_2H_5)_3$	in methanol or	1000	0.57
5	Vinyl trifluoroacetate	None	60	Benzoyl peroxide	methanol-dioxane	4000	0.65

[a] Solid state polymerization to give a stereoblock polymer (8).
[b] A measure of syndiotactic content in poly(vinyl alcohol) (9).

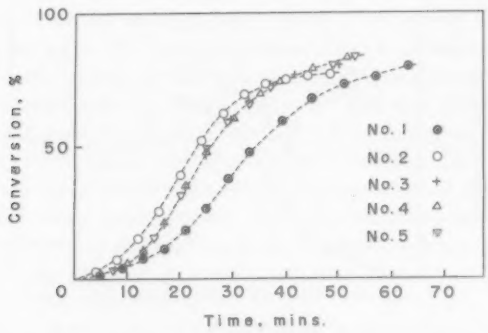

Fig. 1. Hydrolysis of PVAc of various tacticities: (No. 1) isotactic; (No. 2) stereoblock; (No. 3) conventional; (No. 4, 5) syndiotactic.

TABLE II

Rate of Hydrolysis of PVAc of Various Tacticities

Type of tacticity	k_0, mole/liter/min.	m
Isotactic	0.07	110
Stereoblock	0.13	110
Conventional and syndiotactic	0.07	170

formate) (8) is anomalously high while the degree of polymerization (DP) of this polymer is fairly low as compared with those of the other PVAc samples. Although chain length of PVAc has been believed to have little influence on the rate of hydrolysis (6), some reports showed that PVAc of very low DP hydrolyzed at a slightly higher rate (7,10). Because the difference in the rate under discussion here is very minute, effect of the DP of PVAc on the rate has been reexamined. PVAc of low DP hydrolyzed at a somewhat higher rate as shown in Figure 3. Therefore, the higher initial rate of stereoblock PVAc may be primarily attributed to its short chain length.

All PVAc samples derived from vinyl esters polymerized by ordinary free radical initiation gave almost the same time-conversion curve as shown in Figure 1, whereas, poly(vinyl acetal)s derived from these samples had been shown to have different hydrolytic reactivities depending upon the tacticity of the original poly(vinyl alcohol) (1). Thus, the rate of hydrolysis of PVAc is relatively insensitive to the tacticity of the polymer as compared with the rate of hydrolysis of poly(vinyl acetal). The effect of the tactic structure on the rate becomes noticeable only

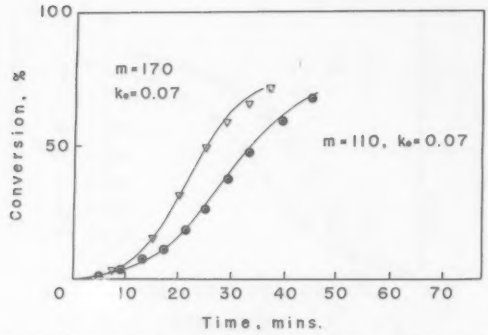

Fig. 2. Comparison of experimental data with curves calculated from the empirical equation.

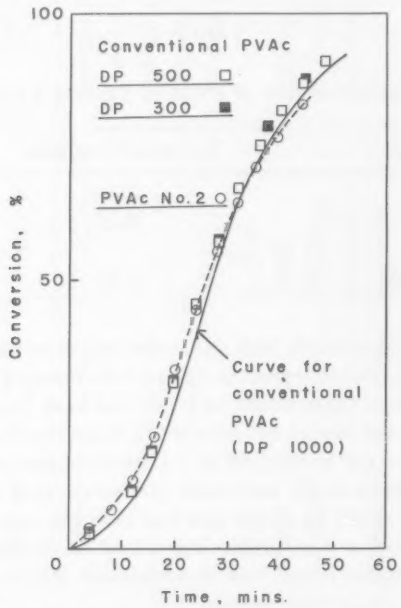

Fig. 3. Effect of chain length of PVAc on the rate of hydrolysis. Experimental conditions were somewhat varied here; concentration of the polymer was 0.012 base mole/liter and that of NaOH was 0.015N. 75% Dioxane/water was used as solvent.

when isotactic sequences longer than some critical length are contained in PVAc samples. Degree of rate acceleration is relatively low in such polymers.

Adsorption of the catalyst on the hydroxyl groups in the polymer has been believed to be the most probable cause of reactivity rise in acetyl groups neighboring to the hydroxyl groups (11). It is therefore very likely that the degree of rate acceleration during the reaction can be influenced by the tactic structure of the polymer. However it is not yet clear why the degree of rate acceleration is less in polymers having isotactic sequences longer than some critical length. This should be interpreted in consideration of the chain conformation of the polymer together with its steric configuration. For the better understanding of the problem, hydrolyses of stereoisomers of pentane-2,4-diacetate and of heptane-2,4,6-triacetate are now being studied. Details of the work will be published in the future.

Note added in proof: A similar difference in hydrolytic reactivity has been substantiated by Prof. I. Sakurada et al., of the Kyoto University for isotactic and syndiotactic PVAc samples essentially identical with those used in this study. (Read at the Annual Meeting of the Soc. Polymer Sci., Japan, Tokyo, May 1963).

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EFFECT OF STEREOSPECIFICITY ON EQUILIBRIUM ACETALIZATION OF POLY(VINYL ALCOHOL) AND OF PENTANE-2,4-DIOL

The rate of hydrolysis of poly(vinyl acetal) has recently been shown to depend upon the tacticity of the original poly(vinyl alcohol) (PVA) samples (1). As is well known, the acetalization of PVA is a reversible reaction. Therefore, a difference in the rate of hydrolysis implies the existence of different equilibrium states in the acetalization of PVA. In this communication, equilibrium acetalization of PVA of various tacticities, and of stereoisomeric pentane-2,4-diols, are reported.

To keep the reaction system homogeneous, hydrolyses of the acetals were conducted in 87.5% (v/v) dioxane/water. Polymerization conditions of the original polymers are given in Table I. They were converted to PVA and then acetalized by following the methods used in previous work (1-4). The degree of acetalization of the products was determined by total hydrolysis of the acetal groups, followed by titration of acetaldehyde with hydroxylamine hydrochloride. These acetalized PVA's of different tacticities and acetals of stereoisomeric pentane-2,4-diols, fractionated by gas chromatography (1,5), were subjected to the equilibrium hydrolysis. Hydrolysis was carried out in a sealed tube containing 5 g./liter of the acetal and 0.02N hydrochloric acid at 60°C. for 24 hr. The amount of acetaldehyde liberated was determined by titration with sodium sulfite (1,6,7). Results are given in Table II.

From data given in Table II, the equilibrium constant K, was calculated for each sample. In the calculation, residual substituents (hydroxyl group) incapable of reaction because of isolation between reacted

TABLE I

Polymerization Conditions of Original Polymers

No.	Monomer (vol.-%)	Medium	Initiator	Temp., °C.
1	Vinyl tert-butyl ether (5)	Toluene	$BF_3(C_2H_5)_2O$	−78
2	Vinyl acetate (50)	Methanol	2,2′-Azobis isobutyronitrile	60
3	Vinyl formate (50)	Methyl formate	$B(C_2H_5)_3$	−78

TABLE II

Equilibrium Hydrolyses of Various Acetals

Original diol		Degree of acetalization, %	
No.	Stereospecificity	Initial	At equilibrium
Pentane-2,4-diol $-\alpha$	meso-Type corresponds to isotactic part	100	86.33
PVA-1	(Isotactic) D_{916}/D_{850}[a] = 0.02	85.4	66.0
PVA-2	(Conventional) D_{916}/D_{850}[a] = 0.42	82.7	55.8
PVA-3	(Syndiotactic) D_{916}/D_{850}[a] = 0.57	77.5	50.6
Pentane-2,4-diol $-\beta$	dl-Type, corresponds to syndiotactic part	100	49.81

[a] A measure of syndiotacticity in PVA (8).

TABLE III

Equilibrium Constant in Acetalization of Various Alcohols

Alcohol	K	K_{cor}
Pentane-2,4-diol (meso-type)	8.70×10^3	
PVA-1		3.01×10^3
PVA-2		1.14×10^3
PVA-3		7.96×10^2
Pentane-2,4-diol (dl-type)	3.70×10^2	

pairs should be considered. As a matter of convenience, a correction for an irreversible system was applied to the system (9).

$$K = [\text{Acetal}]\,[\text{Water}]/[\text{Diol}]\,[\text{Aldehyde}]$$

$$K_{cor} = (2 - X)\,K/2\,(1 - X)$$

where X is a degree of acetalization at equilibrium.

As given in Table III, there is a marked difference in equilibrium constants between the two stereoisomeric diols. Moreover, K_{cor} for PVA varies with the tacticity of the polymer within these two K values. Assuming that K values for meso-type and dl-type pentane-2,4-diols correspond to those for complete isotactic and complete syndiotactic PVA samples, respectively, the degree of tacticity for each PVA sample may be calculated as follows:

PVA-1 $I_0 = 0.746$, $S_0 = 0.254$

PVA-2 $I_0 = 0.470$, $S_0 = 0.530$

PVA-3 $I_0 = 0.329$, $S_0 = 0.671$

Here I_0 and S_0 denote the isotactic and syndiotactic fractions, respectively (10).

Though some problems remain concerning the above assumption and the method of correction for the effect of residual isolated hydroxyl groups on the reaction, studies on the equilibrium state of acetalization should provide quantitative information about the steric structure of PVA. For better understanding of this problem, the acetalization of stereoisomeric heptane-2,4,6-triols is now being studied. Details of the work will be reported in the future.

The authors are greatly indebted to Drs. G. J. Arquette and J. A. Manson of the Air Reduction Company for their kindness regarding the translation to English.

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SOME INFORMATION ON THE RELATIONSHIP BETWEEN STEREOREGULARITY AND WATER RESISTANCE OF POLY(VINYL ALCOHOL)

In 1955, the degree of swelling in water of poly(vinyl alcohol) (PVA) was found to depend upon the polymerization temperature of the original poly(vinyl acetate) (1). Since then, there has been much discussion about the effect of PVA structure, particularly stereostructure, on the water resistance of PVA. It has long been considered that the difference in the swelling degree of different PVA samples becomes negligible when the PVA films are highly crystallized by heat treatment. We have disclosed that, if the swelling test is carried out in hot water, the effect of the stereoregularity on the water resistance of PVA is still remarkable even after crystallization (2). Later, we discussed the interrelation among the stereoregularity, the crystallizability, and the water resistance of PVA (3). Recently, researchers of the Diamond Alkali Company (4) have made some observations which are mainly in accordance with our results (2,3). We have, however, a somewhat different opinion on the water resistance of PVA in relation to the stereoregularity.

Rosen et al. (4) stated that higher stereoregularity does not result in relatively higher crystallinity when the crystallinity is increased by heat treatment, but the relatively higher water resistance is retained. This is primarily in good agreement with our view (2,3), though detailed examinations disclosed that the density of PVA slightly increases with syndiotacticity (5,6) and highly isotactic PVA is much less crystallizable than ordinary PVA (3,7). They supposed that the higher water resistance appears to be related to the stereoregular structure in the amor-

TABLE I

Preparation and Crystallization of PVA Samples

No.	Polymerization		PVA		Heat treatment
	Monomer	Temp., °C.	DP	D_{916}/D_{850} [a]	
I	Vinyl formate	−60	1600	0.54	100°C., 30 min.
II	Vinyl acetate	120	1600	0.35	180°C., 5 min.

[a] A measure of syndiotacticity of PVA (8).

TABLE II

Crystallinity and Water Resistance of PVA Films [a]

No.	Density	X-ray spectra				Water resistance (85°C.)	
		(101) ($10\bar{1}$)	(200)	(002)	(111)	Swelling degree [b]	Solubility %
I	1.2909	S	–	–	W	2.06	22.85
II	1.3041	VS	MW	W	M	∞	100

[a] Cast from aqueous solution, 0.2 mm. thickness.
[b] Weight of water imbibed/weight of PVA film.
[c] S, Strong; M, Middle; W, Weak; V, Very.

phous part. We believe that the water resistance of the crystalline part must be discussed as well as the water resistance of the amorphous part if we are to gain a better understanding of the water resistance of PVA. The following experimental evidence supports this view.

Two PVA samples of different syndiotacticities, whose preparative conditions are given in Table I, were subjected as films to different crystallization treatments. PVA-I, the more syndiotactic polymer, underwent a less rigorous heat treatment than did PVA-II, the less syndiotactic polymer. Consequently, the film of PVA-II, was highly crystallized, while the film of PVA-I was not, as x-ray and density data in Table II clearly show. However, when these two PVA films were immersed in water at 85°C., the more highly crystallized film-II soon dissolved while the less crystallized film-I showed high water resistance.

These results indicate that the crystalline portion, as well as the amorphous portion, should also be considered as a factor in the improvement of water resistance.

As mentioned by Bunn (9), the side chain – OH – in PVA is so small in size that it can be interchangeable with the hydrogen atom in the crystalline lattice. Hence, the stereoregularity has little effect on the fiber pattern of PVA (7,10). However, the arrangement of hydrogen bonding in PVA should be different depending on the tacticity of PVA. In a planar zigzag chain, isotactic configuration favors intramolecular hydrogen bonding while syndiotactic configuration favors interchain hydrogen bonding. Hence the interchain force in the crystalline part may vary with tactic structure of PVA. Consequently, the cohesion of the crystalline portion in PVA may be dependent on the stereoregularity, although no difference can be observed in x-ray examination. The increases in melting point and water resistance of essentially syndiotactic PVA (2) seem to provide experimental verification of this view. The experimental result that isotactic PVA shows only very poor crystalliz-

ability (6,7) also indicates the importance of the interchain hydrogen bonding to the crystallization of PVA.

The authors are greatly indebted to Drs. G. J. Arquette and J. A. Manson of the Air Reduction Company for their kindness regarding the translation to English.

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MOLECULAR WEIGHT DISTRIBUTION OF POLYPROPYLENE OBTAINED BY SOME MODIFIED ZIEGLER-NATTA CATALYSTS

The molecular weight distribution of polypropylene obtained by a Ziegler-Natta type catalyst has not been deeply studied in connection with the catalytic nature. Davis et al., (1) measured molecular weight distribution of polypropylene produced by several types of catalysts and found that the polymers obtained by titanium halide catalysts have broad distribution and those by vanadium halide systems have narrow distribution. Carrick et al., (2) also presented that polyethylene by $SnPh_4$-$AlBr_3$-VCl_4 catalyst has very narrow distribution of molecular weight compared with conventional Ziegler polyethylenes.

Many attempts have been made to modify the catalyst by addition of a third component. The role of these additives, however, has not been completely clarified. In this letter, the effect of the third component on the molecular weight distribution will be disclosed.

Determination of the molecular weight distribution was carried out by a column fractionation method. As the elution medium, a mixture of

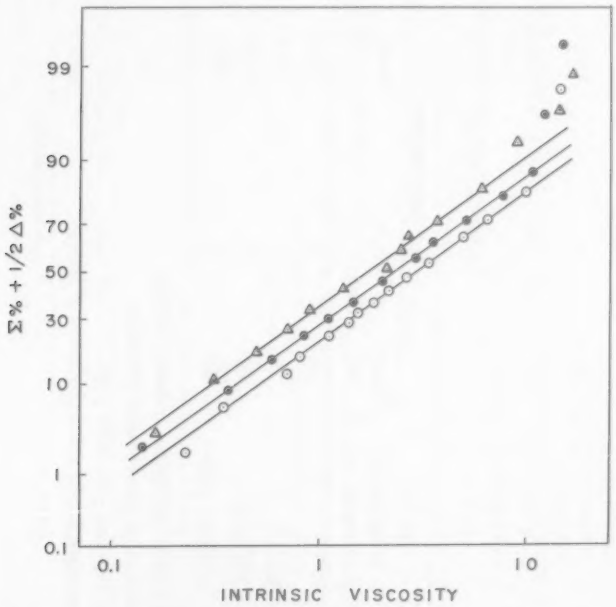

Fig. 1. Probability distribution curve for polypropylene by $AlEt_3$-$TiCl_3$(H) catalyst. (Δ) Control; (●) pyridine; (⊙) HPT.

TABLE I

Polypropylene by $AlEt_3$-$TiCl_3$(H)[a] Catalyst

Expt. No.	Third component of cat.	Polymerization			Heptane extraction, hHIP,[c] %	Mol. wt. $\bar{M} \times 10^{-4}$	Fractionation[d]	
		Temp., °C.	Press. kg./cm.^{2}	Rate, g. P.Pr/g. $TiCl_3$.hr.			M_w/M_n	Polymer recovery, %
1	–	60	5	23.4	78.2	28.0	17.4	99.7
2	HPT[b]	60	5	65.9	93.1	45.8	17.3	92.8
3	Pyridine	60	5	39.7	83.2	36.1	21.3	100.0
4	Ethanol amine	60	5	56.2	85.9	38.5	20.1	100.6

[a] $TiCl_3$(H): hydrogen reduced $TiCl_3$.
[b] Hexamethyl phosphoric triamide.
[c] Hot heptane insoluble part.
[d] Fractionation of total produced polymer.

TABLE II. Polypropylene by $AlEt_2Cl$-$TiCl_3$(AA) [a] Catalyst [b]

Expt. No.	Third component of cat.	Polymerization			Heptane extraction, hHIP, %	Mol. wt. $\bar{M} \times 10^{-4}$	Fractionation	
		Temp., °C.	Press., kg./cm.^{2}	Rate, g. P.Pr/g. $TiCl_3$.hr.			M_w/M_n	Polymer recovery, %
5	–	70	5	117	88.4	13.8	5.9	97.4
6	Tetramethyl thiourea	70	5	74	95.1	11.3	6.6	99.9
7	CS_2	70	5	85	94.9	12.7	6.0	98.0
8	Diglyme [c]	70	5	21	89.7	10.4	6.0	100.4

[a] $TiCl_3$(AA): aluminum reduced, activated.
[b] Molecular weight of polymer was regulated by hydrogen.
[c] Diglyme: diethyleneglycol dimethylether.

TABLE III. Polypropylene by $AlEtCl_2$-$TiCl_3$(HA) [a] Catalyst

Expt. No.	Third component of cat.	Polymerization			Heptane extraction, hHIP, %	Mol. wt. $\bar{M} \times 10^{-4}$	Fractionation	
		Temp., °C.	Press., kg./cm.^{2}	Rate, g. P.Pr/g. $TiCl_3$.hr.			M_w/M_n	Polymer recovery, %
9	Triethyl amine	70	5	20.8	92.2	21.8	44.8	100.8
10	Tetramethyl urea	70	5	7.3	94.5	24.7	32.4	101.0

[a] $TiCl_3$(HA): hydrogen reduced, activated.

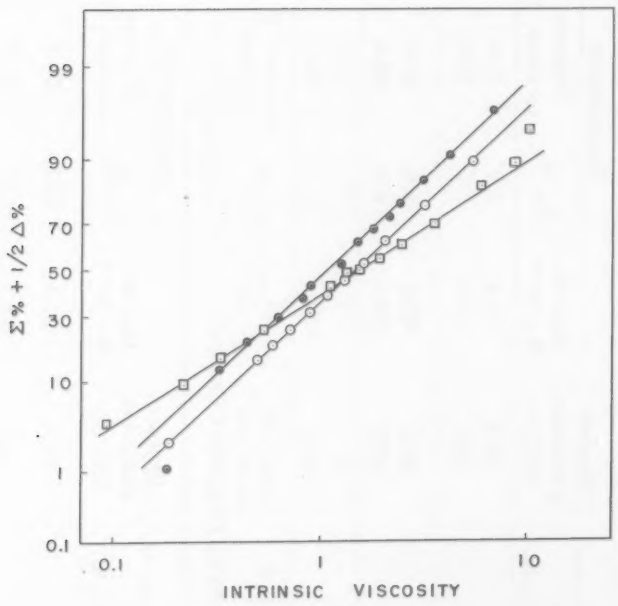

Fig. 2. Probability distribution curve for polypropylene by $AlEt_2Cl$-$TiCl_3$(AA) and $AlEtCl_2$-$TiCl_3$(HA) catalyst systems. (●) $AlEt_2Cl$-$TiCl_3$(AA)-diglyme; (⊙) $AlEt_2Cl$-$TiCl_3$(AA) control; (⊡) $AlEtCl_2$-$TiCl_3$(HA)-NEt_3.

tetralin and ethyl carbitol was used and the latter contained 25 vol. % of ethylene glycol. If pure ethyl carbitol was used, a part of low molecular weight polymers was undesirably dissolved into nonsolvent. Thus, 1 g. of polypropylene sample was placed into a three-necked flask with hard glass sand, whose particle size was between 100 and 150 meshes. In nitrogen atmosphere, the polymer was dissolved at 180°C. into tetralin containing 0.1% Topanol CA and 0.1% TPL (Thiodipropionic acid dilauryl ester) as stabilizers. After cooling at a steady rate, the mixture of polymer and sand was transferred into a fractionation column. Fractionation was carried out at 180°C. using the stabilizers mentioned above. The flow rate of the solvent was 120 ml./hr.

Three catalyst systems, i.e., $AlEt_3$-$TiCl_3$(H), $AlEt_2Cl$-$TiCl_3$(AA), and $AlEtCl_2$-$TiCl_3$(HA) were chosen and various kinds of additional components were used as modifiers of the catalyst. Some of the components show very interesting behaviors in the polymerization. The data for the polymerization and the fractionation are given in Tables I-III. When the catalyst $AlEt_3$-$TiCl_3$(H) is modified by N-containing compounds such as pyridine, HPT (hexamethyl phosphoric triamide), and

ethanol amine, the polymerization activity and the isotactic yield of polymer are greatly improved. In the case of $AlEt_2Cl$-$TiCl_3$(AA) system, some kinds of sulfur compounds, i.e., tetramethyl thiourea and CS_2, bring about the highest isotactic yields. Diglyme, one of O-containing compounds, considerably retards the polymerization reaction. The two component catalyst system $AlEtCl_2$-$TiCl_3$(HA) produces atactic low molecular weight polymer accompanied by a small amount of isotactic polymer, but by addition of triethylamine or tetramethyl urea the isotactic yield and polymerization activity are exceedingly raised.

Figures 1 and 2 show Wesslau's plot of fractionation results described in the tables. It is indicated that Wesslau's relation fits well up to 90% of cumulative weight and it should be valid to estimate the molecular weight distribution by the value of M_w/M_n, which is calculated from the slope of Wesslau's line.

Among the polymers using the catalyst system: $AlEt_3$-$TiCl_3$(H)-third component, Wesslau's lines are practically parallel and M_w/M_n values fall between 17 and 21. In the catalyst system $AlEt_2Cl$-$TiCl_3$(AA), since the molecular weight of polymer was too high, a quantity of hydrogen was added to regulate it. As shown in Table II, the polymers produced have narrow molecular weight distribution. The M_w/M_n values are 5-7 and not affected by the third component of the catalyst. The distribution of polymers by the system of $AlEtCl_2$-$TiCl_3$(HA)-third component (Table III) is broad and M_w/M_n values are 30-50.

From the experimental results, it may be concluded that, as long as the same combination of organometallic compound and transition metal halide is used, M_w/M_n values of polymers by modified catalysts agree within the experimental error and the third component of catalyst scarcely affects the molecular weight distribution. It may be inferred that the third component does not alter the nature of the catalyst but only modifies it. On the other hand, a different catalyst combination gives different distribution. Detailed data and discussion on this problem will be published later.

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ELECTROCHEMICAL PROPERTIES OF IONOGENIC MEMBRANES PREPARED BY THERMAL AND OXIDATIVE DEGRADATION OF POLY(VINYL ALCOHOL)

Poly(vinyl alcohol), PVA, degraded under the mild conditions of 110°C. in air had electrochemical properties indicative of low concentrations of ionogenic groups (1). This account presents the properties of PVA membranes after degradation under the more severe conditions of 175 ± 5°C. in a stream of dry oxygen.

The PVA, a high viscosity, greater than 99% alkaline hydrolyzed polymer (Du Pont Elvanol, Grade 72-60), was filtered, dialyzed, and reprecipitated from water solution prior to preparing the casting solution. The membranes were cast on glass sheets from a water solution to produce a dry thickness of 20 ± 3 μ.

Concentration potentials using KCl and HCl as the electrolyte solutions were measured at 30 ± .05°C. using cells of the type,

$$\text{Ag, AgCl} \mid \text{KCl } (a_1^{\pm}) \mid \text{membrane} \mid \text{KCl } (a_2^{\pm}) \mid \text{AgCl, Ag}$$

where $a_1^{\pm}$ and $a_2^{\pm}$ are the mean ionic activities and the ratio $a_1^{\pm}/a_2^{\pm} = 3.00 \pm .04$. The apparatus used was similar to that employed by Scatchard and Helfferich (2) with the stirring accomplished by pumping the electrolyte solutions against the membrane at 150 ± 10 ml./min. For a given membrane and pair of solutions the measured e.m.f. was reproducible within ±0.2 mv. Concentration potentials of a strong acid membrane, AMFion C-103C, were measured to compare with the PVA membranes. Procedures similar to those previously described (1) were used to determine the osmotic flow, thickness and resistance of the membranes. The osmotic flow measurements were made against 1.0M sucrose at 30 ± .05°C. and no leakage of sucrose across the membrane was detected. A simple conductivity cell was used in which the membrane, with a cross section of 2.14 cm.^{2}, separated two solution compartments equipped with platinized platinum electrodes. The cell resistance was measured with a Wheatstone bridge operated at 1000-cycles/sec. The cell was maintained at 30 ± .05°C. and 0.1M KCl was used in the two compartments. The reported specific conductivities, L, were calculated by the equation suggested by Helfferich (3),

$$L = d/A(R - R_0) \qquad (1)$$

where d = thickness of the membrane, A = membrane cross section, and $(R - R_0)$ = difference in resistance of the cell with and without the

membrane. Reproducibility between membranes heated the same length of time was within 5% for the specific conductivities and osmotic flow rates. Equilibration periods of as long as 5 days were required before constant measurements of the concentration potentials and resistances could be obtained.

Degradative reactions of PVA which appear possible under the experimental conditions are: unsaturation, chain scission and crosslinking, increased crystallinity, and oxidation to ketone and carboxylic acid groups (4-6). The degradation produced an amber color in the membranes and increased their wet strength and brittleness when dry. The significant change in the infrared spectra of the membranes during degradation was the development of absorption in the carbonyl ($\sim$1700 cm.$^{-1}$) and alkene ($\sim$1600 cm.$^{-1}$) regions. A portion of the carbonyl absorption was due to the presence of carboxylic acid groups since treatment with a KOH solution reduced the absorption in the 1700 cm.$^{-1}$ region and produced strong absorption in the carboxylate group regions, 1600 and 1400 cm.$^{-1}$. Figure 1 illustrates these spectral changes. Chain scission is necessary for the formation of carboxylic acid groups, unless they are formed only at the chain-end positions. The absorption band at 1141 cm.$^{-1}$ which is attributed to the degree of crystallinity (7) increased during the initial period of the degradation. The degradation apparently produced carboxylic acid groups and a more rigid membrane structure despite possible chain scission. These modifications decreased osmotic flow and specific conductance, and increased concentration potentials of the membranes. Table I summarizes the values obtained.

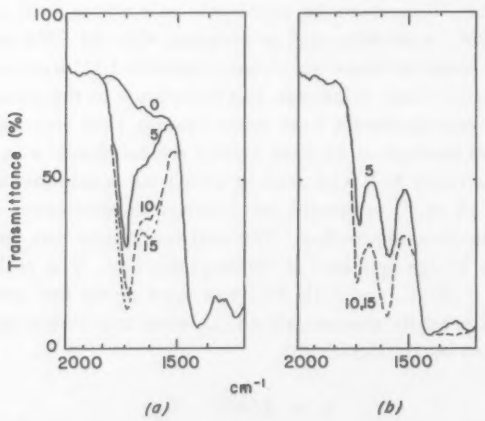

Fig. 1. (a) Effect of degradation on spectra of PVA in the 1300 to 2000 cm.$^{-1}$ region. Hours heated indicated on curves. (b) Spectra after treating degraded PVA membranes with 0.1N KOH.

TABLE I

Values of Concentration Potentials, Specific Conductance and Osmotic Flow Rates

Membrane	Heat treatment (hr.)	Concentration potentials in mv. for activity pairs, $a_1^{\pm}/a_2^{\pm}$ .1500/.0500	.0500/.0167	.0167/.00557	.00557/.00186	L (ohm^{-1} cm.$^{-1}$ $\times 10^4$)	Osmotic flow rate (λ hr.$^{-1}$ cm.$^{-1}$)
		KCl solutions					
PVA	5	48.50	54.60	56.01	56.25	1.03	21.21
PVA	10	51.70	55.80	55.95	55.39	.53	8.72
PVA	15	50.64	55.30	56.29	55.36	.26	3.25
AMFion C–103C	0	55.20	56.96	56.56	56.63		
		HCl solutions					
PVA	5	54.22	55.60	56.90	57.71		
AMFion C–103C	0	56.64	57.63	57.78	57.79		

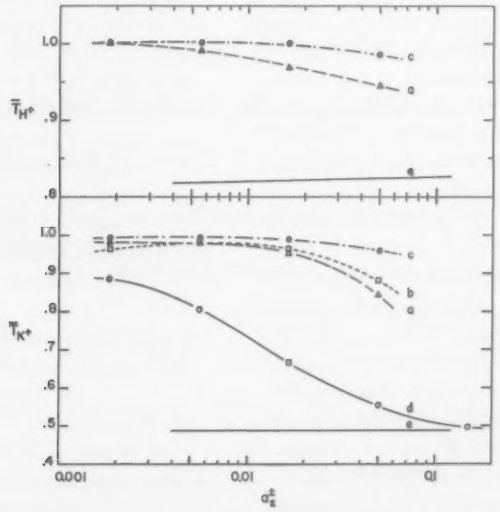

Fig. 2. Cation transport numbers vs. the mean ionic activity of the more dilute of the solution pairs, $a_2^{\pm}$. (a) PVA heated 5 hr. at 175°C. in oxygen; (b) PVA heated 15 hr. at 175°C. in oxygen; (c) AMFion C–103C; (d) PVA heated 84 hr. at 110°C. in air, from reference (1); (e) cation transport numbers in water, from reference (8).

The cation transport numbers were estimated using the modified Nernst equation:

$$e = (2\overline{T}_+RT/F)\ 10^3 \ln (a_1^{\pm}/a_2^{\pm}) \qquad (2)$$

where e = e.m.f. of the cell in mv., $\overline{T}_+$ = cation transport number in the membrane, and R, T and F have their usual meaning. The dependence of the calculated values of $\overline{T}_+$ on the mean ionic activity is presented in Figure 2. The PVA membranes subjected to severe degradation, with $\overline{T}_+$ greater than 0.95 at activities below 0.02, exhibited greater selectivity than the membrane degraded under mild conditions.

In summary, manageable, weak-acid membranes with high selectivity over a limited concentration range were prepared by severe thermal and oxidative degradation of PVA.

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